REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Papers	

4. TITLE AND SUBTITLE

Please see attached

5a. CONTRACT NUMBER F04611-98-C-0010

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER 62203F

6. AUTHOR(S)

5d. PROJECT NUMBER 1011

5e. TASK NUMBER 00NM

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-TP-2000-205

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Leilani Richardson
a. REPORT	b. ABSTRACT	c. THIS PAGE	A		19b. TELEPHONE NUMBER *(include area code)*
Unclassified	Unclassified	Unclassified			(661) 275-5015

101100nm 4041 ✓

MEMORANDUM FOR PRS (Contractor/In-House Publication)

FROM: PROI (TI) (STINFO) 24 Oct 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-205**
Suri, Suresh; Tinnierllo, M. & Marcischak, J. (ERC), "Synthesis and Screeniing of Advanced Hydrocarbon Fuels"

2000 USAF High Energy Density Matter (HEDM) Contractors Conference (Statement A)
(Park City, UT, 24-26 Oct 2000) (Deadline: PAST)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
Comments:_____
_____
_____

Signature _____ Date _____

2. This request has been reviewed by the Public Affairs Office for: a.) appropriateness for public release and/or b) possible higher headquarters review
Comments: _____
_____
_____

Signature _____ Date _____

3. This request has been reviewed by the STINFO for: a.) changes if approved as amended, b.) appropriateness of distribution statement, c.) military/national critical technology, d.) economic sensitivity, e.) parallel review completed if required, and f.) format and completion of meeting clearance form if required
Comments:_____
_____
_____

Signature _____ Date _____

4. This request has been reviewed by PRS for: a.) technical accuracy, b.) appropriateness for audience, c.) appropriateness of distribution statement, d.) technical sensitivity and economic sensitivity, e.) military/ national critical technology, and f.) data rights and patentability
Comments:_____
_____
_____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

_____
PHILIP A. KESSEL Date
Technical Advisor

Cleared (PA)_____
Logged (PA)_____
Notified (PA)_____
Copied & Distributed (STINFO)_____
This original is for PA files

Synthesis & Screening of Advanced Hydrocarbon Fuels

Suresh C. Suri*, Michael Tinnirello[1]& Jacob Marcischak[1]

**Air Force Research Laboratory/PRSP; [1]ERC Inc.*

10 East Saturn Blvd., Edwards Air Force Base, CA 93536

Presentation Outline

- **Goal**
  - HEDM program
  - NASA program
  - IHPRPT program (propellant perspective)
- **Criteria for fuel selection**
- **Approach**
- **Results**
- **Accomplishments** (FY-2000)
- **Planned Efforts** (FY-2001)

HEDM Goal

- **To Develop fuels with increased Isp over LOX/RP-1**
  - LOX/RP-1 (Calculated Isp) = 300 sec
  - LOX/RP-1 (Delivered Isp) = 263 sec

Determined at sea level and 1000 psi chamber pressure

IHPRPT GOAL
(PropellantContribution)

To Meet IHPRPT Phase II and Phase III Objective

Phase	Time	Improvement Over SOTA* Isp (del)
II	2005	+ 5 Sec
III	2010	+ 11 Sec

*SOTA: LOX/RP-1 Propellant Isp(del) = 263 Sec.
Isp (calc) = 300 Sec.

NASA Goal

- **FY-1999**
  - Deliver three advanced hydrocarbon fuel in 8-10 lb quantity.
    - Quadricyclane
    - 1,7-Octadiyne
    - Bicyclopropylidene
- **FY-2000**
  - Screen four hydrocarbons for their physical and hazardous properties.

Criteria for Fuel Selection

- **Predicts better performance (Isp) over LOX/RP-1 system**
- **Most desirable physical properties**
  - Lower vapor pressure compared to RP-1
  - Higher density (≥ RP-1 = 0.801 g/ml)
  - Freezing point (≤ -10 °C; RP-1 = -41.4 °c)
  - Boiling point ≥ B. P. Of RP-1
- **Storable**
- **Compatible with the current system**

Approach

- **Structural requirements**
- **Survey of energetic hydrocarbons**
- **Selection of hydrocarbons based on improved theoretical performance**
- **Synthesis of target hydrocarbons at bench scale.**
  - *Easy preparation, cost effective and safe*
- **Translate bench-scale synthesis to pilot scale.**

Heat of Formation of Saturated Hydrocarbons

Compound	Structure	ΔHf (Obs)
Ethane	CH_3CH_3	-20.04
Propane	$CH_3CH_2CH_3$	-25.02
Butane	$CH_3(CH_2)_2CH_3$	-30.03
Pentane	$CH_3(CH_2)_3CH_3$	-35.08

- $\Delta Hf/\text{added } CH_2 = \sim -5$ Kcal/mole

Heat of Formation of Unsaturated Hydrocarbons

Compound	Structure	ΔHf(Obs)
Ethylene	$CH_2=CH_2$	+12.5
1,3-Butadiene	$CH_2=CH-CH=CH_2$	+26.11
	ΔHf/C = ~ +6.25 Kcal/mole	
Acetylene	$HC\equiv CH$	+54.36
	ΔHf/C = ~ + 27.1 Kcal/mole	

Structural Requirement for High Energy Contents (Cont..)

- The energy content is also increased by incorporating strain in the molecule

– Ring compound	ΔHf
– Cyclopropane	+ 12.73 kcal/mole
– Cyclobutane	+ 6.78 kcal/mole
– Cyclopentane	- 18.44 kcal/mole

Structural Requirements For High Energy Contents (Summary)

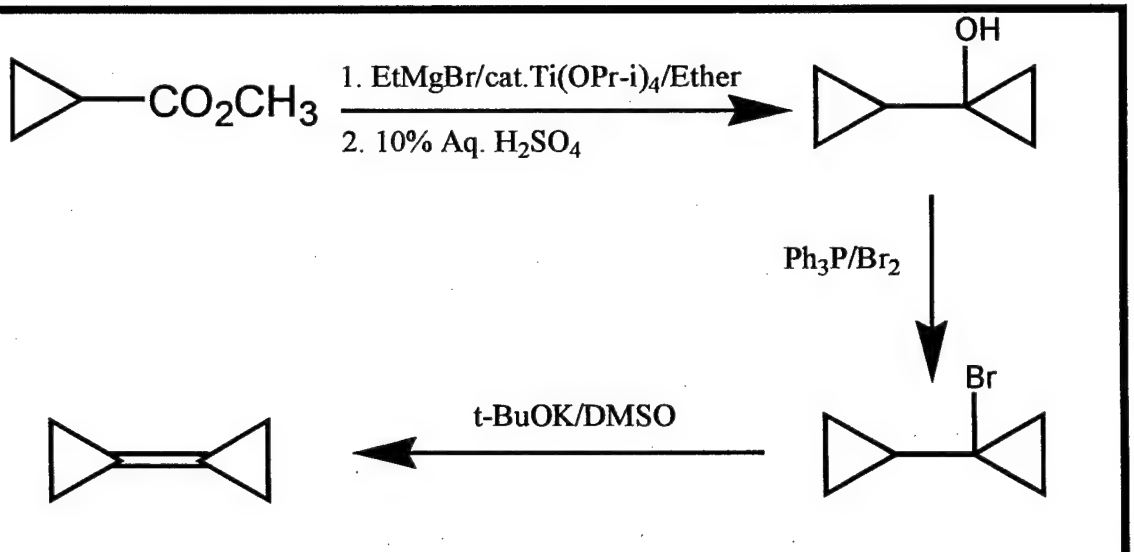
Incorporation of small ring (strain) and unsaturation in a molecule increases its energy contents

Performance Comparison of Energetic Hydrocarbons (Theoretical)

Hydrocarbons	H/C ratio	Density (g/ml)	Calc. ΔHf (Kcal/mole)	Calc. Isp (sec)
RP-1	1.9	0.80	-5.76	300.0
Quad	1.14	0.98	72.2	307.0
BCP	1.33	0.85	76.1	312.5
AFRL-1	1.2	0.77	64.0	311.3
AFRL-2	1.25	0.87	73.4	307.2
AFRL-3	1.0	0.93	123.6	307.2
AFRL-4	1.0	-	129.6	321.4
AFRL-5	1.33	0.80	56.3	308.7

Results

Synthetic Sequence of BCP



1. A.de Meijere, S. I. Kozhushkov, T. Spaeth and N. S. Zefirov; *J. Org. Chem.* **1993**, 58, 502
2. S.C. Suri; *Technical Report PL-TR-97-3057*, **1997**, p 26

Characterization of BCP

Physical properties

B.P. = 101 °C

M.P. = -12 °C

F.P. = -6.4 °C

Density = 0.8454 g/ml

ΔHf (exp.) = 67.4 kcal/mole

ΔHf (calc.) = 76.1 kcal/mole

Hazardous properties

Zero card gap (negative)

Drop test > 200 kg/cm

Friction test 133 newton

Toxicity

(Inhalation LC50)

1.95 mg/L

Adiabatic Compression(psi)

3000	Neg.

Is BCP Hypergolic?

- **Qualitative Test**
  - BCP is found to be hypergolic using nitrogen tetroxide(NTO). Spontaneous reaction with visible flame.
  - Hypergolic with inhibited red fuming nitric acid (IRFNA) as oxidizers. (Darren M. Thompson, U.S. Army missile command).
- **Ignition Delay**
  - The work is in progress under SBIR phase-1 with TDA Research, Inc.

Synthesis of AFRL-1

- Two steps synthesis
- Involves readily available materials
- Yield in both steps is > 90 %

Characterization of AFRL-1

Physical Properties

B.P. = 52- 55 °C

Density = 0.77 g/ml

ΔHf (Exp.)= 67.4 Kcal/mole

ΔHf (Calc.)= 64.0 Kcal/mole

Hazardous Properties

"0" card gap (Negative)

Liq. Impact test > 200 Kg-cm

Friction Test 78 Newtons

Adiabatic Compression (psi)

3000	Neg.

Synthesis of AFRL-3

- One step synthesis from AFRL-1.
- Requires oxidative coupling of AFRL-1.
- Yield is 92 %.

Characterization of AFRL-3

Physical Properties

B.P. = 102 °C

M.P. = -13 °C

Density = 0.93 g/ml

ΔH_f (Calc.)= 123.6 kcal/mole

ΔH_f (Exp.)= 117.0 kcal/mole

Hazardous Properties

- "0" card gap (negative)
- Liq Impact test <20 kg-cm
- Friction Test = 64.8 Newton

Adiabatic Compression(psi)

500	Neg.
2000	Neg.
3000	Neg.

Synthesis of AFRL-5

- Higher homologue of AFRL-1
- Two step synthesis
- Yield in both steps is greater than 90 %

Characterization of AFRL-5

Physical properties

B.P. = 78 °C

M.P. = -92.8 °C

Density = 0.7957 g/ml

ΔH_f (Exp.) = 50.39 kcal/mole

ΔH_f (Calc.) = 56.3 kcal/mole

Hazardous properties

"0"card gap (TBD)

Liq. Impact Test > 200 kg-cm

Friction Test = 43.12 newton

Adiabatic Compression (psi)

3000	Neg.

Accomplishments (FY 00)

- Delivered four hydrocarbons to NASA/Marshall.
  - Cyclopropyl acetylene (AFRL-1).
  - Bicyclopropylidene
  - Quadricyclane
  - 1,7-Octadiyne
- Synthesized two advanced hydrocarbons(AFRL-1 & AFRL-3) at bench-scale level.
- 200 gm of AFRL-3 was synthesized in the laboratory.

Planned Efforts of Fiscal Year 2001 (Technical)

- To continue exploring bench scale synthesis of advanced hydrocarbon (AFRL-4).
- Evaluate physical & hazardous properties of AFRL-4 & AFRL-2.

Alliances

- **Industry**
  - Boeing
  - TRW
  - Kistler
  - Aerojet
- **NASA**
  - Marshall
  - Glenn
- **DOD**
  - Navy- China Lake
  - Army- Huntsville

Team Efforts

Research

- Suresh C. Suri
  Michael Tinnirello
  Jacob Marcischak

Theoretical Efforts

- Jeffrey Mills

Physical Properties

- Paul Jones, JoAnne Larue, Jeff Yinn

Hazardous Properties

- Tommy W. Hawkins, Adam Brand, Milton Mckay, Ismail Ismail

Acknowledgement

Financial Support

- Air Force Office of Scientific Research (AFOSR)
- National Aeronautics and Space Administration (NASA)/MSFC